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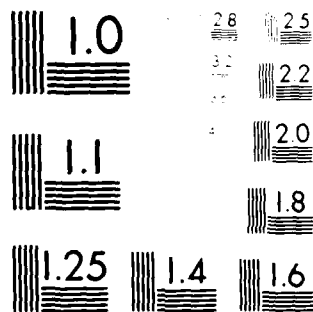
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TECHNICAL REPORT NO. 27

Investigations of Nebulizer Techniques
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by

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Investigations of Nebulizer Techniques
for Direct Determination of Metals in
Lubricating Oils by ICP

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Abstract

Equipment and procedures are described which allow the analysis of metals in lubricating oils without the need for dilution or other sample pretreatment. A sample heater has been added to a modified Babington principle nebulizer. This nebulizer is capable of producing, from undiluted oils, aerosols which are suitable for introduction into an Inductively Coupled Plasma Atomic Emission Spectrophotometer. Heating the samples immediately prior to nebulization greatly increases the output of aerosol, and also reduces variations in output due to differences in sample viscosity. The type of organometallic complex used in the preparation of standards is shown to be unimportant if the region of the plasma which is observed is well chosen.

INTRODUCTION

The analysis of used lubricating oils for metallic impurities is important in the implementation of sound maintenance programs for oil-lubricated equipment. Such analyses have been used in maintaining a variety of equipment (1-6). The U. S. Air Force estimates that a savings of \$13 to \$15 million per year is realized through the Spectrometric Oil Analysis Program (SOAP) (7).

The method used for wear metal analysis should be simple, rapid, and capable of determining several elements simultaneously. Currently, the method of choice is rotating electrode spark source spectroscopy (8), which offers high throughput and simultaneous multielement determinations. Atomic absorption spectrophotometry (AAS) may also be used to determine metal concentrations in oils (1, 2, 4-7); however, the technique requires more sample preparation than does spark spectroscopy, and instruments capable of simultaneous multielement determinations by AAS are not available. Interferences due to the type of organometallic complex used in the preparation of standards for use in AAS analyses have been reported in both the air-acetylene and the nitrous oxide-acetylene flames (9-11). Recent reports (12,13) have indicated that Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is potentially a better technique than either spark source spectroscopy or AAS. A disadvantage of ICP-AES is the need to dilute the samples in a low viscosity solvent prior to analysis. This dilution is required to achieve nebulization of viscous samples, and to make the nebulization efficiency equal for samples of varying viscosity. While achieving these aims, the dilution also reduces the overall sensitivity of the analysis, degrades the limit of detection, and

adds an opportunity for contamination or analyst error.

The Babington principle nebulizer is capable of handling viscous and particulate laden samples (14), making it attractive for use with oil samples. Fry (15) demonstrated the production of aerosols from undiluted lubricants with this type of nebulizer; however, the rate of aerosol production was low and was strongly affected by the sample viscosity.

In this study, a modification of the Babington principle nebulizer is investigated as a means to circumvent the dilution step required by conventional systems. A variety of studies are presented which demonstrate the ability of the nebulizer to be used in conjunction with an ICP-AES for the direct determination of metals in lubricating oils.

EXPERIMENTAL

Apparatus

The nebulizer assembly is depicted in Figure 1. The body was 5.1 cm diameter plexiglass tubing with a teflon end cap. Both the orifice tip and the sample delivery tube were fitted with brass blocks containing electrical resistance heaters. The heaters were driven by variable autotransformers, and the temperatures of the heater blocks were monitored by thermocouples. A third thermocouple was introduced into the oil stream below the orifice tip to measure the temperature of the oil.

The tip had a 0.20 mm diameter orifice, producing a sample gas flow of 1 L/min when operated at 30 psi.

A 45° angle in the nebulizer body directed the aerosol upward into the ICP torch, and also collected the larger drops of sample. Further aerosol

refinement, provided by a 25 cm length of 5.1 cm diameter plexiglass tubing interposed between the nebulizer and the torch base, contributes to stable operation of the ICP discharge.

The ICP-AES system comprised a 3 tube concentric torch with an extended coolant tube, driven through a matching network by a linear amplifier excited at 27.12 MHz, a 0.35 m monochromator, and a microcomputer for system control and data acquisition. The instrument has been described in detail elsewhere (16, 17).

Two pumps were used to deliver samples to the nebulizer. For the sensitivity versus temperature work, a single speed peristaltic pump was used. Because the output of this pump varied from 6 to 20 ml/min, depending upon the sample viscosity, a stepper motor driven syringe pump employing disposable syringes was constructed, and was used for all further work. The syringe pump could deliver samples at rates from 1 to 80 ml/min reproducibly and without regard for sample viscosity.

Procedures

The system operating conditions are given in Table 1. Except where noted, the syringe pump was operated at 5 ml/min. The 3 cm observation height was just above the edge of the coolant tube.

Net signals were reported by subtracting the observed signal at the background correction wavelength from the signal measured at the analytical wavelength.

The emission sensitivity was measured as a function of sample temperature for several commercially available motor oils, and the sensitivities observed for iron in a series of samples prepared from different fresh oils were compared.

The effect of varying the sample flowrate was investigated.

Conostan 245 base oil (Continental Oil Co., Ponca City, OK), and a variety of motor oils purchased locally were used to prepare samples. Iron-containing samples were prepared in 50g batches by gravimetric dilution of Conostan oil soluble Fe standard in the various oils to a concentration of 100 µg/g. The recommended level of Conostan stabilizer was added to each sample. The samples were stirred for 20 minutes with gentle heating and were allowed to cool before use.

Standards for an observation height study were prepared by dissolving appropriate amounts of nickel 2,4-pentanedionate (nickel acetylacetonate; NiAA), nickel cyclohexanebutyrate (NiCHB), iron 2,4-pentanedionate (FeAA), Conostan nickel standard (NiCON) or Conostan iron standard (FeCON) in 10 ml of pyridine and bringing them to 100 ml with mixed xylenes. These solutions contained 100 µg/ml. NiAA, NiCHB, and FeAA were obtained from the Alfa Division of Thiokol (Danvers, MA).

RESULTS AND DISCUSSION

Effect of Sample Temperature

The iron emission intensity was measured as a function of sample temperature for a range of weights (viscosities) of Pennzoil brand motor oil, and for several brands of SAE 30W oil. These data are shown in Figures 2 and 3.

As seen in Figure 2, the temperature profile curves have a sigmoid shape, and a relatively low slope at a sample temperature of 70°C. The emission signal is increased by a factor of 10 to 50 when the temperature is raised from 25°C to 70°C.

These data are plotted in Figure 4 as values relative to the signal observed for Pennzoil 30W. This figure shows that the difference in the emission

intensity among the various oils is markedly decreased at elevated temperatures, and that the amount of scatter in the data is also decreased with temperature. The reduction in the scattering is due to an improvement in the signal to noise ratio at high temperature.

Sensitivity in Various Oils

To better demonstrate the intensity equalizing effect of the sample heater, studies were performed to compare the sensitivities obtained for iron in various oils. For this series of investigations, the more reproducible and stable syringe pump was used, and the data were corrected for drift in the sensitivity of the instrument. A single temperature, 75°C, was used throughout.

Table II gives the emission intensity observed for each oil expressed as a value relative to the emission observed from a sample of Conostan 245 base oil. Eight samples were within 5% of the base oil and the remaining 3 were within 10%. Two samples were prepared without Conostan stabilizer to test for interference from the stabilizer. No effect was observed.

Effect of Type of Organometallic on Sensitivity

A potential interference which has been observed in AAS (9-11) was studied in the ICP. This interference results from a variation in response, dependent on the type of organometallic used in standard preparation.

Figure 5 shows the effect of the type of complex utilized to solubilize iron in oil upon the emission intensity observed as a function of observation height. At low observation heights (near the load coil), a difference in signal level is found between the two iron compounds used. At heights above 20 mm, the compounds both yield the same signal intensity. The nickel compounds, which gave different sensitivities by AAS (10, 11) were found to produce identical emission intensities when observed 30 mm above the load coil.

The ICP technique is free from this type of matrix interferences as reported for AAS when the plasma is observed well above the load coil. This agrees with previous observations that the high temperature environment of the ICP reduces the severity of some interferences which are observed in AAS (18). For the experimental system employed here, this viewing region also yields optimum signal to background ratios.

Effect of Sample Flowrate

Low sample flowrates into the nebulizer produce the highest emission intensities, as shown in Figure 6. It is possible that flows below the minimum used in this study might produce optimum sensitivity; however, an excessively long memory results from lower flowrates. At 1.3 ml/min, approximately 1.5 minutes are required after changing samples for the signal level to stabilize.

CONCLUSIONS

Equipment and methodology have been developed which allow undiluted oil samples to be nebulized into an Inductively Coupled Plasma with a minimal effect of viscosity upon nebulization efficiency. The use of the ICP eliminates certain matrix interferences which are observed in AAS.

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TABLE I
Operating Conditions

Frequency	27.12 MHz
Forward Power	2 KW
Coolant Ar Flow	19 L/min
Plasma Ar Flow	2 L/min
Sample Ar Flow	1 L/min
Observation Height Above Load Coil	3 cm
Analytical Wavelength, Fe	259.9 nm
Background Correction Wavelength, Fe	260.2 nm
Analytical Wavelength, Ni	231.6 nm
Background Correction Wavelength, Ni	233.9 nm
Bandpass	0.1 nm
Nebulizer Pressure Drop	30 psi

TABLE II

Relative Emission Intensities Observed for
Iron in a Variety of Motor Oils at a Sample
Temperature of 75°C.^{a/}

Sample Identification	Relative Intensity
Conostan 245 Base Oil	1.00
Pennzoil 10W	1.01
Pennzoil 20W w/o Stabilizer	0.99
Pennzoil 20W	0.97
Pennzoil 30W w/o Stabilizer	1.01
Pennzoil 30W	1.04
Pennzoil 40W	0.90
Pennzoil 50W	0.96
Ray-Lube 30W	0.89
Valvoline 30W	0.93
Kendall 40W	0.93
Quaker State 30W	1.04

^{a/} Conostan 245 is defined as a relative intensity of 1.00

FIGURE CAPTIONS

Figure 1 Modified Babington Principle Nebulizer with Sample Heater. (a) sample inlet; (b) heater; (c) heater block; (d) gas inlet; (e) drain; (f) body; (g) teflon spacer; (h) support.





Figure 2 Emission Intensity as a Function of Temperature for Various Grades of Pennzoil HD Motor Oil.  :20W;  :30W;  :40W;  :50W.






Figure 3 Emission Intensity as a Function of Temperature for Various Brands of 30W Motor Oil.  :Valvoline;  :Pennzoil;  :Quaker State;  :Ray Lube;  :Kendall GT-1 (40W).








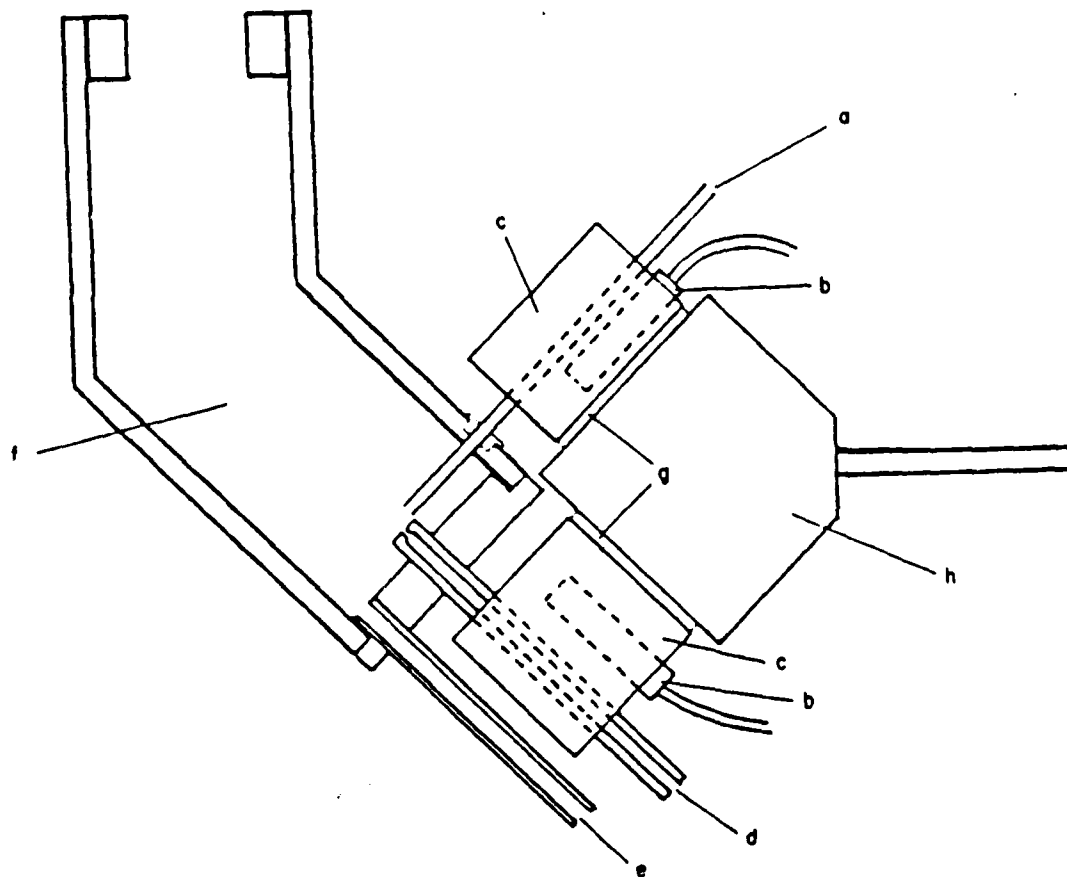
Figure 4 Ratios of Emission Intensities Given by Various Oils to the Intensity Measured for Pennzoil 30W at the Same Temperature.  :Pennzoil 20W;  :Pennzoil 40W;  :Pennzoil 50W;  :Ray Lube 30W;  :Quaker State 30W;  :Valvoline 30W;  :Kendall GT-1 40W.

Figure 5 Ratio of the Emission Intensities Given by FeAA and FeCON as a Function of Observation Height.

Figure 6 Emission Intensity as a Function of the Rate of Flow of Sample into the Nebulizer.

Fig. 1



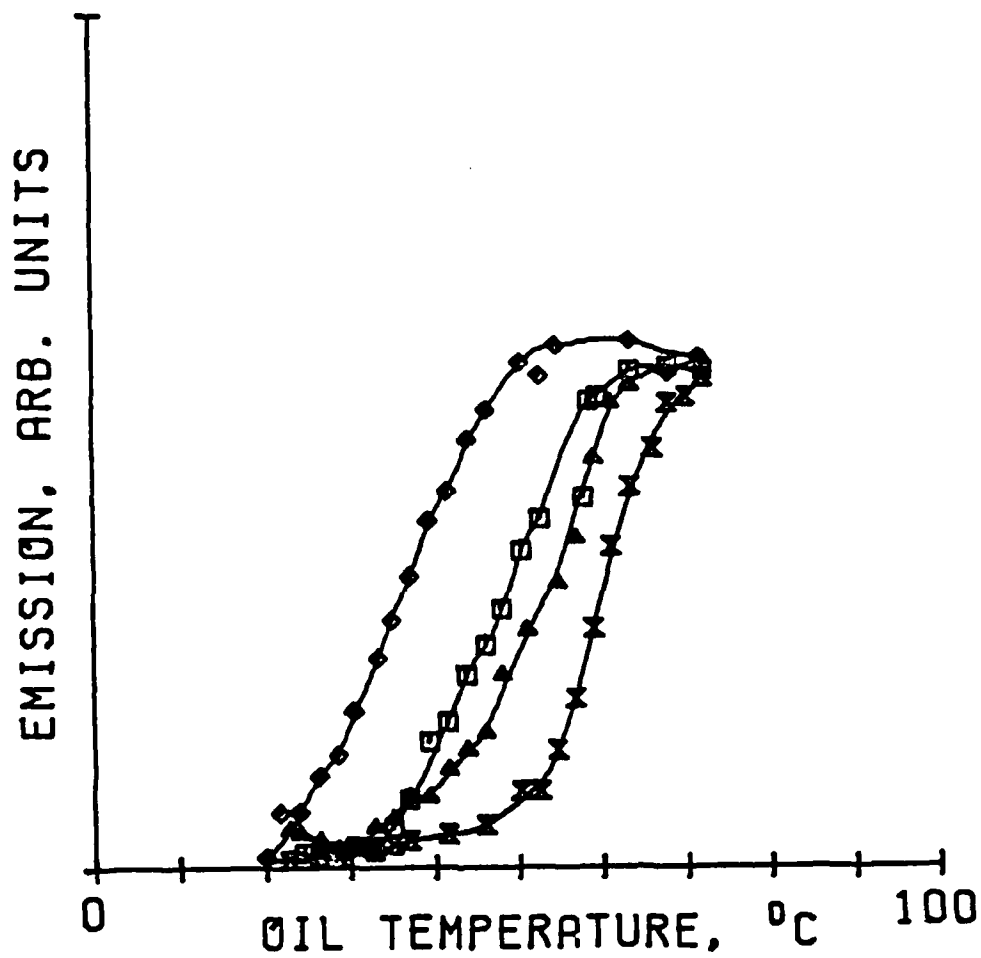
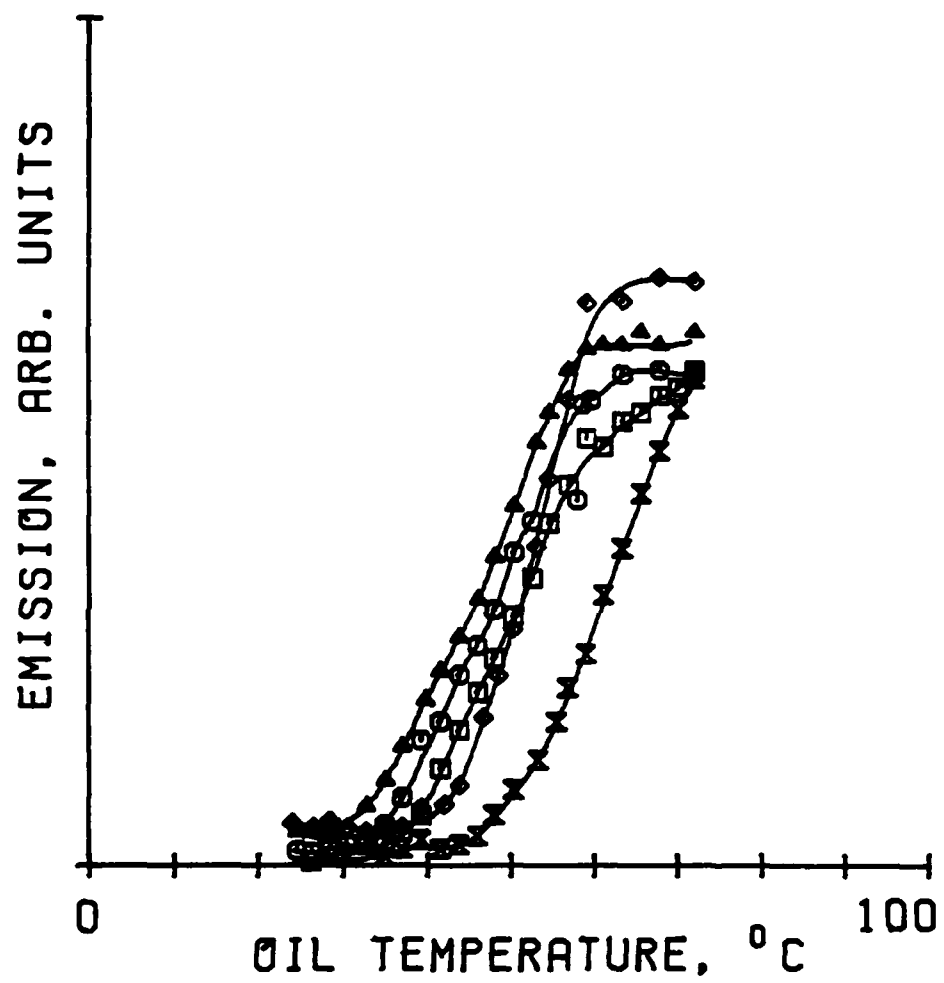
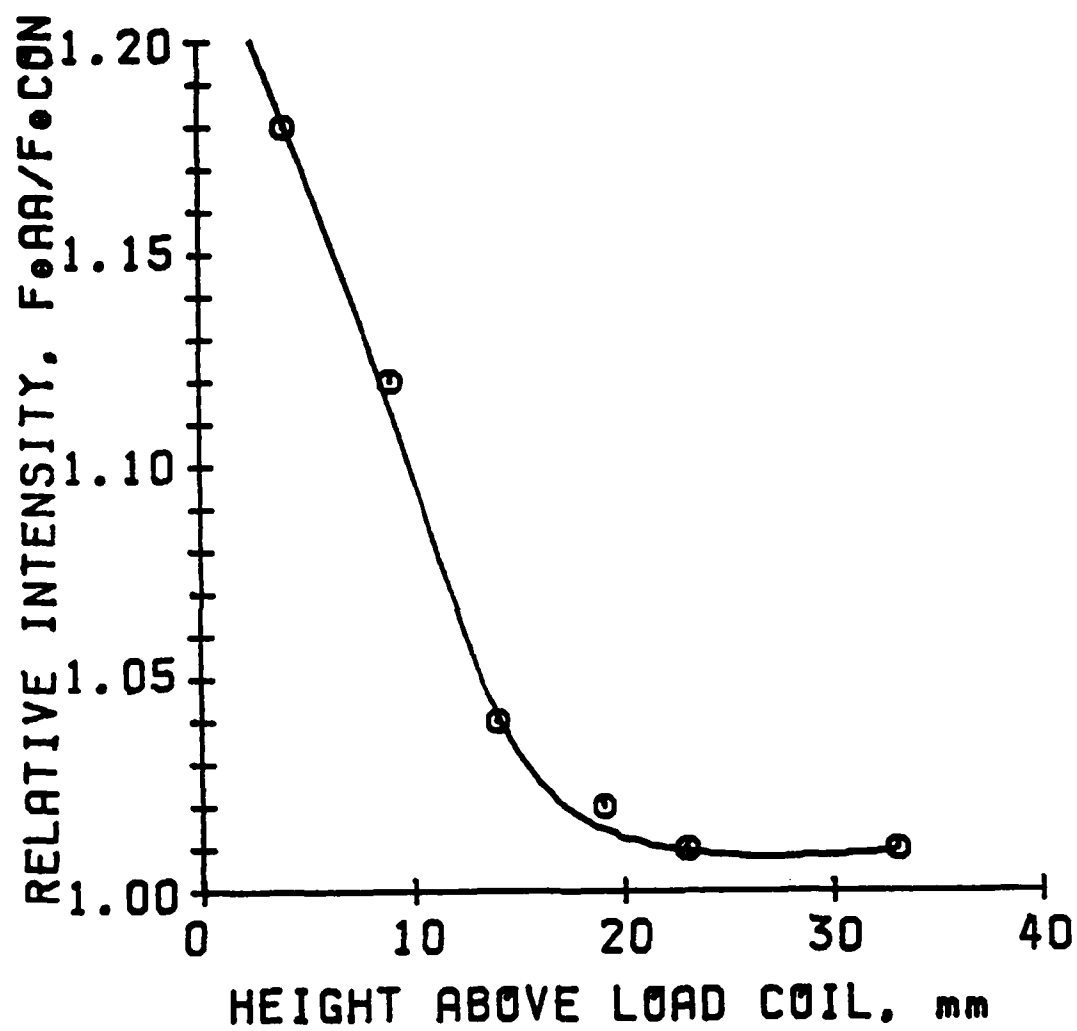


FIGURE 2. EMISSION INTENSITY AS A FUNCTION OF TEMPERATURE
FOR VARIOUS GRADES OF PENNZOIL MOTOR OIL.
20W, 30W, 40W,
50W.





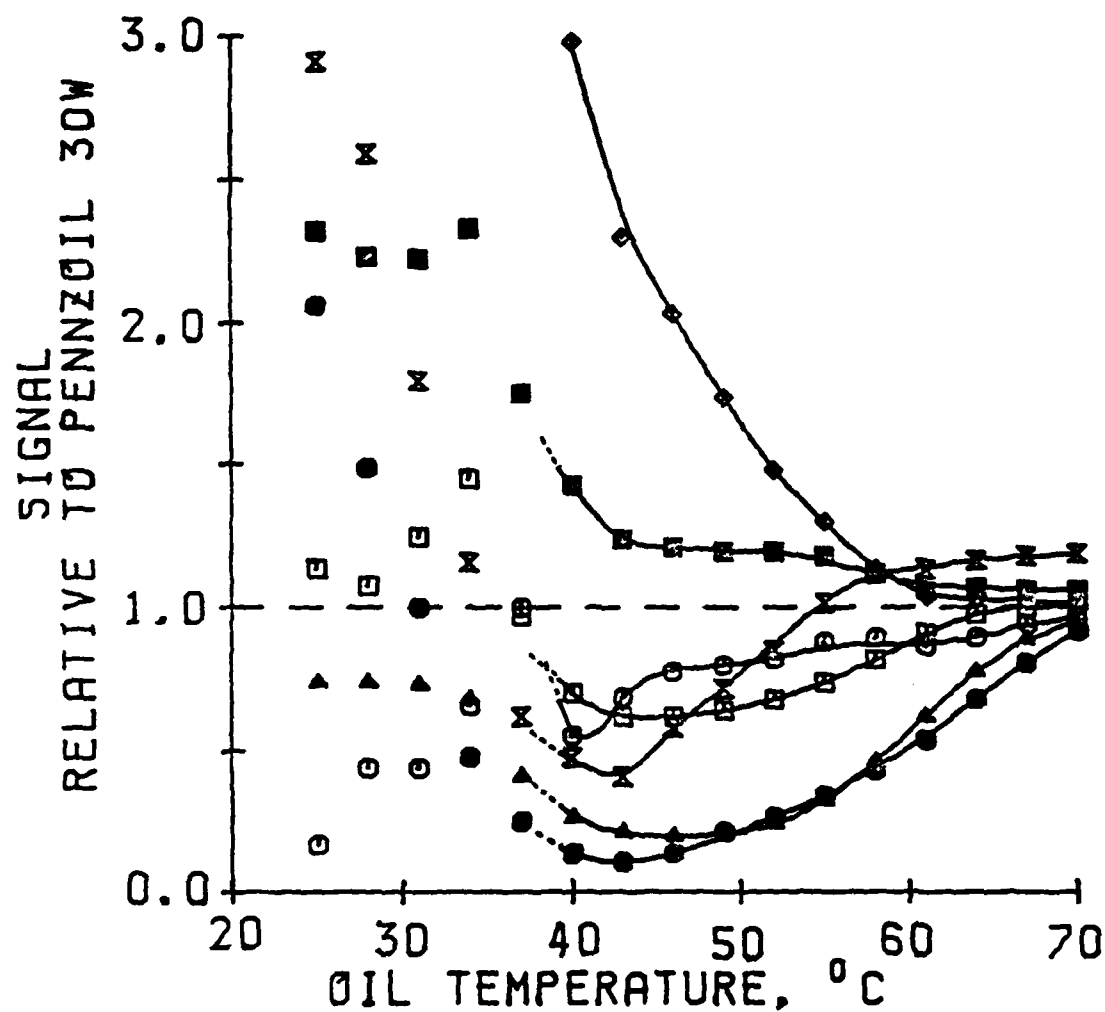


FIGURE 4. RATIOS OF EMISSION INTENSITIES GIVEN BY VARIOUS OILS TO THE INTENSITY MEASURED FOR PENNZOIL 30W AT THE SAME TEMPERATURE.

PENNZOIL 20W,	
PENNZOIL 40W,	PENNZOIL 50W,
RAY-LUBE 30W,	QUAKER STATE 30W,
VALVOLINE 30W,	KENDALL GT-L 40W.

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